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PTO/SB/05 (4/98)
Approved for use through 09/30/2000. OMB 0651-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No.	PC-3201
First Inventor or Application Identifier	G.D. SMITH
Title	Advanced High Temperature Corrosion Resistant Alloy
Express Mail Label No.	TB896941276US

jc542 U.S. PTO 09/148749 09/04/98

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231

1. [X] * Fee Transmittal Form *(e.g., PTO/SB/17)* *(Submit an original and a duplicate for fee processing)*
2. [X] Specification [Total Pages 16] *(preferred arrangement set forth below)*
   - Descriptive title of the Invention
   - Cross References to Related Applications
   - Statement Regarding Fed sponsored R & D
   - Reference to Microfiche Appendix
   - Background of the Invention
   - Brief Summary of the Invention
   - Brief Description of the Drawings *(if filed)*
   - Detailed Description
   - Claim(s)
   - Abstract of the Disclosure
3. [ ] Drawing(s) *(35 U.S.C. 113)* [Total Sheets]
4. Oath or Declaration [Total Pages]
   - a. [X] Newly executed (original or copy)
   - b. [ ] Copy from a prior application (37 C.F.R. § 1.63(d)) *(for continuation/divisional with Box 16 completed)*
     - i. [ ] DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

5. [ ] Microfiche Computer Program *(Appendix)*
6. Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all necessary)*
   - a. [ ] Computer Readable Copy
   - b. [ ] Paper Copy (identical to computer copy)
   - c. [ ] Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. [X] Assignment Papers (cover sheet & document(s))
8. [ ] 37 C.F.R.§3.73(b) Statement *(when there is an assignee)* [ ] Power of Attorney
9. [ ] English Translation Document *(if applicable)*
10. [X] Information Disclosure Statement (IDS)/PTO-1449 [X] Copies of IDS Citations
11. [ ] Preliminary Amendment
12. [ ] Return Receipt Postcard (MPEP 503) *(Should be specifically itemized)*
13. [ ] * Small Entity Statement(s) *(PTO/SB/09-12)* [ ] Statement filed in prior application, Status still proper and desired
14. [ ] Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
15. [ ] Other: .....

16. **If a CONTINUING APPLICATION,** *check appropriate box, and supply the requisite information below and in a preliminary amendment:*

[ ] Continuation [ ] Divisional [ ] Continuation-in-part (CIP) of prior application No: _____/_____

Prior application information: Examiner _____ *Group / Art Unit:* _____

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

17. CORRESPONDENCE ADDRESS

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Signature		Date	9/4/98

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FEE TRANSMITTAL

Patent fees are subject to annual revision on October 1. These are the fees effective October 1, 1997.
Small Entity payments must be supported by a small entity statement, otherwise large entity fees must be paid. See Forms PTO/SB/09-12. See 37 C.F.R. §§ 1.27 and 1.28.

TOTAL AMOUNT OF PAYMENT ($) 830.00

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	G.D. SMITH
Examiner Name	
Group / Art Unit	
Attorney Docket No.	PC-3201/USA

METHOD OF PAYMENT (check one)

1. ☐ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

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Deposit Account Name

☐ Charge Any Additional Fee Required Under 37 C.F.R. §§ 1.16 and 1.17

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	790	201	395	Utility filing fee	790.00
106	330	206	165	Design filing fee	
107	540	207	270	Plant filing fee	
108	790	208	395	Reissue filing fee	
114	150	214	75	Provisional filing fee	

SUBTOTAL (1) ($) 790.00

2. EXTRA CLAIM FEES

	Extra Claims		Fee from below	Fee Paid
Total Claims		-20** =		X =
Independent Claims		- 3** =		X =
Multiple Dependent				=

**or number previously paid, if greater; For Reissues, see below

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	22	203	11	Claims in excess of 20
102	82	202	41	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	82	209	41	** Reissue independent claims over original patent
110	22	210	11	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 0

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet.	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	950	217	475	Extension for reply within third month	
118	1,510	218	755	Extension for reply within fourth month	
128	2,060	228	1,030	Extension for reply within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,320	241	660	Petition to revive - unintentional	
142	1,320	242	660	Utility issue fee (or reissue)	
143	450	243	225	Design issue fee	
144	670	244	335	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	40.00
146	790	246	395	Filing a submission after final rejection (37 CFR 1.129(a))	
149	790	249	395	For each additional invention to be examined (37 CFR 1.129(b))	

Other fee (specify) _____

Other fee (specify) _____

* Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($) 40.00

SUBMITTED BY				Complete (if applicable)	
Typed or Printed Name	BLAKE T. BIEDERMAN			Reg. Number	34,124
Signature		Date	9/4/98	Deposit Account User ID	

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ADVANCED HIGH TEMPERATURE CORROSION RESISTANT ALLOY

FIELD OF THE INVENTION

This invention relates to the field of nickel-base alloys possessing resistance to high temperature corrosive environments.

BACKGROUND OF THE INVENTION

Nickel-base high temperature alloys serve in numerous applications, such as, regenerators, recuperators, combustors and other gas turbine components, muffles and furnace internals, retorts and other chemical process equipment and transfer piping, boiler tubing, piping and waterwall aprons and waste incineration hardware. Alloys for these applications must possess outstanding corrosion resistance to meet the long life requirements becoming critical in new facility design and operation. While virtually all major industrial equipment is exposed to air on one surface or at one part of the unit, the internal surfaces can be exposed to very aggressive carburizing, oxidizing, sulfidizing, nitriding, or combinations of these corrodents. Consequently, maximum corrosion resistance to the broadest possible range of aggressive high temperature environments, is a long-sought aim of the metallurgical industry.

Traditionally, these alloys rely on precipitation hardening from a combination of γ' [Ni_3 (Al, Ti)], γ'' [Ni_3(Nb, Al, Ti)], carbide precipitation and solid solution strengthening to give the alloy strength. The γ' and γ'' phases precipitate as stable intermetallics that are essentially coherent with the austenitic-fcc matrix. This combination of precipitates significantly enhances the high temperature mechanical properties of the alloy.

It is an object of this invention to provide an alloy that possesses resistance to carburizing, oxidizing, nitriding and sulfidizing environments.

It is a further object of this invention to provide an alloy with sufficient phase stability and mechanical integrity for demanding, high temperature applications.

SUMMARY OF THE INVENTION

A nickel-base alloy consisting of, in weight percent, 42 to 58 nickel, 21 to 28 chromium, 12 to 18 cobalt, 4 to 9.5 molybdenum, 2 to 3.5 aluminum, 0.05 to 2 titanium, at least one microalloying agent selected from the group consisting of 0.005 to 0.1 yttrium for carburization resistance and 0.01 to 0.6 zirconium for sulfidation resistance, 0.01 to 0.15 carbon, 0 to 0.01 boron, 0 to 4 iron, 0 to 1 manganese, 0 to 1 silicon, 0 to 1 hafnium, 0 to 0.4 niobium, 0 to 0.1 nitrogen, incidental impurities and deoxidizers.

DESCRIPTION OF PREFERRED EMBODIMENT

A high temperature, high strength alloy characterized, in part, by a unique combination of microalloying elements to achieve extremely high levels of corrosion resistance in a broad spectrum of aggressive environments. A nickel base of 42 to 58 weight percent provides an austenitic matrix for the alloy. (This specification expresses all alloy compositions in weight percent.) An addition of 12 to 18 weight percent cobalt enhances the corrosion resistance of the alloy and contributes solid solution strengthening to the matrix. This matrix has sufficient corrosion resistance to tolerate up to 4 weight percent iron, up to 1 weight percent manganese and up to 1 weight percent silicon without a substantial decrease in corrosion resistance. Allowing iron, manganese and silicon into the alloy facilitates the recycling of nickel-base alloys. Furthermore, manganese may benefit the alloy by tying up trace amounts of sulfur. In addition, the alloy may contain

incidental impurities such as oxygen, sulfur, phosphorus and deoxidizers such as calcium, magnesium and cerium.

An addition of 21 to 28 weight percent chromium imparts oxidation resistance to the alloy. Chromium levels less than 21 weight percent are inadequate for oxidation resistance; levels above 28 weight percent can produce detrimental chromium-containing precipitates. An addition of 4 to 10 weight percent molybdenum contributes to stress corrosion cracking resistance and contributes some solid solution strengthening to the matrix. Aluminum in an amount ranging from 2 to 3.5 weight percent contributes to oxidation resistance and can precipitate as γ' phase to strengthen the matrix at intermediate temperatures. Most advantageously, the matrix should contain at least 2.75 weight percent aluminum for excellent oxidation resistance.

For sulfidation resistance, it is critical that the alloy contain a minimum of 0.01 weight percent zirconium to stabilize the scale against inward migration of sulfur through its protective scale layer. Zirconium additions above 0.6 weight percent adversely impact the alloy's fabricability. Advantageously, an addition of at least 0.005 weight percent yttrium improves both oxidation and nitridation resistance of the alloy and is critical to establish carburization resistance. Yttrium levels above 0.1 increase the cost and decrease the hot workability of the alloy. Only when optimum levels of chromium, aluminum and critical microalloying levels of yttrium and zirconium are present in the alloy will outstanding corrosion resistance be achieved in the complete spectrum of carburizing, oxidizing, nitriding and sulfidizing environments. However, where only carburizing and oxidizing corrosion resistance is required, the microalloying with zirconium can be omitted from the composition. Where only sulfidizing and oxidizing corrosion resistance is required, yttrium can be omitted from the composition. Maximum overall corrosion resistance is achieved by a combination containing at least 2.75 weight percent aluminum, 0.01 weight percent zirconium and 0.01 weight percent yttrium.

The optional elements of 0 to 1 weight percent hafnium and 0 to 0.1 weight percent nitrogen stabilize the oxide scale to contribute toward oxidation resistance. Hafnium in the amount of at least 0.01 weight percent and nitrogen in the amount of at

least 0.01 weight percent each serve to increase oxidation resistance. Excess hafnium or nitrogen levels deteriorate the mechanical properties of the alloy.

An addition of 0.05 to 2 weight percent titanium will act like the aluminum addition and contributes to the alloy's high temperature mechanical properties by precipitating as γ' phase. Most advantageously, γ' phase consists of 8 to 20 weight percent of the alloy. Maintaining niobium at less than 0.4 percent enhances the alloy's stability by limiting the amount of metastable γ'' precipitated. Most advantageously, γ'' consists of less than 2 weight percent of the alloy. An addition of at least 0.01 percent carbon strengthens the matrix. But carbon levels above 0.15 weight percent can precipitate detrimental carbides. Optionally, a boron addition of at least 0.0001 weight percent boron enhances the hot workability of the alloy. Boron additions above 0.01 weight percent form excess precipitates at the grain boundaries.

A combination of cobalt, molybdenum and chromium with microalloying additions of titanium and zirconium achieve the unexpected corrosion resistance for multiple environments. The overall compositional range is defined as "about" the following ranges:

TABLE 1

Element	Broad Range[1]	Intermediate Range[1]	Narrow Range[1]	Nominal Range
Al	2 - 3.5	2.25 - 3.5	2.5 - 3.5	2.75 - 3.5
B	0 - 0.01	0.0001 - 0.01	0.001 - 0.009	0.003 - 0.008
C	0.01 - 0.15	0.01 - 0.14	0.01 - 0.12	0.02 - 0.1
Co	12 - 18	12.5 - 17.5	13 - 17	14 - 16
Cr	21 - 28	21.5 - 27	22 - 27	22 - 26
Fe	0 - 4	0 - 3	0.1 - 2.5	0.5 - 2
Hf	0 - 1	0 - 0.8	0 - 0.7	0 - 0.5
Mn	0 - 1	0 - 0.8	0 - 0.6	0 - 0.4
Mo	4 - 9.5	4.5 - 9	5 - 8.5	5 - 8
N	0 - 0.1	0.00001 - 0.08	0.0001 - 0.05	0.01 - 0.05
Nb	0 - 0.4	0 - 0.3	0 - 0.25	0 - 0.2
Ni	42 - 58	43 - 57	44 - 56	45 - 55
Si	0 - 1	0.01 - 0.7	0.02 - 0.5	0.05 - 0.4
Ti	0.05 - 2	0.06 - 1.6	0.08 - 1.2	0.1 - 1
Y	0.005 - 0.1	0.01 - 0.08	0.01 - 0.07	0.01 - 0.06
Zr	0.01 - 0.6	0.01 - 0.5	0.02 - 0.5	0.02 - 0.4

[1]Contains at least one of yttrium for carburization resistance or zirconium for sulfidation resistance.

Alloys 1 to 9 of Table 2 represent heats of the invention; Alloys A to D represent comparative heats.

TABLE 2
(WEIGHT PERCENT)

Alloy	C	Mn	Fe	Si	Ni	Cr	Nb	Al	Ti	Co	Mo	Zr	Other
1	0.08	<.01	1.08	0.12	49.86	24.13	0.016	3.04	0.32	15.05	6.14	0.018	B 0.007
2	0.08	<0.01	1.07	0.12	49.33	23.94	0.020	3.07	0.32	14.94	6.10	0.042	B 0.004 Y 0.019 Hf 0.42
3	0.034	0.008	1.06	0.16	49.58	24.10	0.023	3.34	0.28	15.04	6.11	0.012	B 0.0004 Y 0.030
4	0.08	<.01	1.07	0.12	49.72	24.06	0.017	3.08	0.30	15.06	6.14	0.21	B 0.005 N 0.03
5	0.08	<.01	1.08	0.12	49.71	24.06	0.021	3.03	0.36	15.05	6.18	0.21	B 0.004 Y 0.032 N 0.032
6	0.08	<.01	1.23	0.10	51.07	22.33	0.036	3.02	0.36	15.28	6.31	0.02	Y 0.017
7	0.08	<.01	1.02	0.12	49.66	24.14	0.029	3.07	0.34	15.06	6.19	0.21	B 0.005 N 0.025
8	0.036	0.008	1.08	0.17	49.43	24.10	0.017	3.36	0.31	15.03	6.08	0.01	B 0.0006 Y 0.049
9	0.09	<0.01	1.15	0.11	49.67	24.03	0.023	3.05	0.34	15.01	6.22	0.033	B 0.0037 Y 0.018 Hf 0.09
10	0.08	<.01	1.10	0.12	49.92	24.12	0.022	3.03	0.33	15.00	6.13		B 0.005 Y 0.24
11	0.08	<.01	0.08	0.12	50.91	24.09	0.024	3.05	0.31	15.04	6.13		B 0.004 Y 0.016
12	0.09	<.01	1.09	0.12	49.93	24.08	0.020	3.04	0.32	15.05	6.14		Y 0.036
13	0.05	0.01	1.06	0.10	49.36	24.04	0.019	2.40	0.30	15.12	6.16		Y 0.027
A	0.05	0.01	1.16	0.15	52.40	24.02	0.001	0.88	0.32	14.92	6.08	--	--
B	0.06	0.01	1.06	0.14	51.51	24.01	0.001	1.06	0.33	15.14	6.20	--	--
C	0.05	0.01	1.06	0.13	50.05	24.06	0.001	3.02	0.32	15.10	6.18	--	--
D	0.035	0.007	1.04	0.13	49.33	24.16	0.006	3.12	0.34	15.06	6.12		B 0.006

5 MECHANICAL PROPERTIES

Components constructed from the alloy possess the strength necessary for mechanical integrity and the required stability necessary to retain structural integrity for high temperature corrosion applications. Alloy 13 is typical of the alloy's strength properties. The composition was vacuum melted and cast as a 25 kilogram heat. Part of the heat was soaked at 1204°C and hot worked to 7.6 mm x 127 mm x length slab with intermediate anneals at 1177°C/20 minutes/air cooled and then cold rolled to 0.158 mm x 127 mm x length. A second portion of the heat was hot bar rolled from a 1204°C furnace preheat to 22.2 mm diameter bar with a final anneal at 1177°C/20 minutes/air cooled. Table 3 presents the tensile properties of alloy 13 for selected temperatures to 982°C. Stress rupture strength data for the screening test condition of 982°C/41.4 MPa are given in Table 4. The effect of aging at 760°C/100 hours on room temperature tensile strength and Charpy impact strength are presented in Table 5.

Table 3
Tensile Properties as a Function of Temperature for Alloy 13

Temperature (°C)	0.2% Yield Strength (MPa)	Ultimate Tensile (MPa)	Elongation (%)
RT	584	981	44.3
538	467	733	48.0
649	534	760	38.0
760	494	577	12.0
871	379	437	12.0
982	84.1	119	109.0

Table 4
Stress Rupture Strength Values for Selected Alloys (982°C/41.4 MPa)

Alloy	Life (Hours)	Elongation (%)	Reduction in Area (%)
1	10.2	60.0	47.0
4	12.3	43.1	38.0
6	20.1	62.6	58.7
7	20.1	62.6	58.7
11	10.4	43.7	36.3
12	14.7	44.6	45.8

Table 5 Effect of Aging on RT Tensile Properties of Selected Alloys 1177°C/1 Hour/Air Cool					
Alloy	ASTM Grain Size Number	0.2 %Yield Strength (MPa)	Ultimate Tensile (MPa)	Elongation (%)	Charpy Impact Strength (J)
5	7	606	1072	31.4	80
C	2	528	894	52.9	228
D	2	565	939	49.3	278
After Aging at 760°C/100 Hours/Air Cool					
5	7	810	1239	21.4	45
C	2	669	1074	25.7	31
D	2	681	1089	30.7	29

OXIDATION RESISTANCE

High temperature alloys, a priori, must possess outstanding oxidation resistance. Retorts, muffles, piping and reactors, all too often, while internally containing a hot reactive process stream are exposed externally to air and, consequently, oxidation. Many process streams are oxidizing in nature as well, damaging the internals of gas turbines, boilers and power generation components. The oxidation resistance of the range of compositions of this patent application is exemplified by the oxidation data of Tables 6 and 7. The testing was done using 0.76 mm diameter x 19.1 mm length pins in an electrically heated horizontal tube furnace using an air atmosphere plus 5 percent water vapor by weight. The specimens were cycled to RT at least weekly for weighing. The mass change (mg/cm^2) data versus time to 5,000 hours at 1100°C are given in Table 6 and for times to 5,784 hours at 1200°C in Table 7. Clearly aluminum contributes significantly to oxidation resistance in this range of compositions. Compare Alloys A and B with the compositions of this patent application at 1100°C. Note the progressive increase in oxidation resistance at 1200°C with the increase in aluminum content and the further enhancement afforded by the microalloying in alloys 7 and 8. Scale integrity at 1100°C has been enhanced as shown by the positive mass changes (no apparent loss of chromium by evaporation or spallation) by the additions 190 ppm yttrium, 420 ppm zirconium and 420 ppm hafnium of Alloy 2, by the additions of 320 ppm yttrium, 2100 ppm zirconium and 320 ppm nitrogen of Alloy 5 and by the addition of 270 ppm yttrium to alloy 13. This enhancement is maintained at 1200°C as depicted in Table 7.

5

Table 6 Oxidation Resistance in Air Plus 5% Water Vapor at 1100°C for Times to 5,000 Hours Mass Change (mg/cm^2) Time (Hours) – Cycled Weekly					
Alloy	1,000	2,000	3,000	4,000	5,000
1	-5.75	-8.45	-8.61	-8.62	-8.80
2	0.80	1.00	1.25	1.36	1.41
4	-5.58	-6.52	-6.84	-7.25	-7.80
5	0.78	0.94	1.11	1.18	1.22
6	-4.94	-4.76	-4.72	-4.65	-4.82
7	-8.80	-11.58	-11.93	-12.15	-12.78
9	-1.43	-1.36	-1.29	-1.14	-1.25
10	-6.15	-7.38	-7.62	-7.76	-8.00
11	-3.38	-3.64	-3.90	-4.20	-4.57
12	-4.59	-6.73	-6.97	-7.25	-7.82
13	0.86	0.93	0.21	0.23	0.18
A	-1.85	-7.72	-12.41	-19.87	-37.38
B	-3.53	-9.56	-17.91	-28.88	-48.41
C	1.38	1.76	-1.86	-1.66	-1.56

Table 7 Oxidation Resistance in Air Plus 5% Water Vapor at 1200°C for Times to 5,784 Hours Mass Change (mg/cm^2)				
Time (Hours)	Alloy A	Alloy D	Alloy 3	Alloy 8
168	-4.05	-9.82	-0.58	-0.60
480	-11.97	-10.27	-0.61	-0.38
816	-21.97	-10.30	-0.32	-0.20
1176	-45.75	-10.51	-0.40	-0.22
1872	-269.48	--	--	--
3864	--	-13.86	0.92	-0.80
5784	--	-39.66	-2.29	-1.59

10 **CARBURIZATION RESISTANCE**

Carburization resistance is of paramount importance for certain high temperature equipment, such as, heat treating and sintering furnace muffles and internal hardware, selected chemical reactors and their process stream containment apparatus and power

15 generation components. These atmospheres can range from purely carbonous (reducing)

to highly oxidizing (as seen in gas turbine engines). Ideally, a corrosion resistant, high temperature alloy should be able to perform equally well under both reducing and oxidizing carburizing conditions. Alloys of the compositional range of this application possess excellent carburization resistance under both extremes of oxygen potential. These tests were conducted in electrically heated mullite tube furnaces in which the atmospheres were generated from bottled gases which were electronically metered through the capped furnace tubes. The atmospheres, prior to reacting with the test specimens, were passed over reformer catalysts (Girdler G56 or G90) to achieve equilibrium of the atmosphere. The flow of the atmospheres through the furnace was approximately 150 cc/minute.

Table 8
Carburization Resistance in Two
Carburization Atmospheres at 1,000°C for 1,008 Hours

Mass Change (mg/cm^2)

Alloy	H_2 - 1%CH_4	H_2 – 5.5%CH_4 - 45%CO_2
1	0.38	11.87
2	0.78	10.32
4	0.55	4.14
6	0.26	10.60
7	0.58	15.52
9	0.41	13.13
10	1.11	12.06
11	1.94	10.29
12	2.06	15.35
A	6.57	22.05

SULFIDATION RESISTANCE

Sulfidation resistance can be critical for hardware components exposed to certain chemical process streams, gas turbine combustion and exhaust streams, coal combustion and waste incineration environments. Scale penetration by sulfur can lead to nickel sulfide formation. This low melting point compound can cause rapid disintegration of nickel-containing alloys. It was discovered that alloys containing a minimum of about 0.015% (150 ppm) zirconium are unexpectedly extremely resistant to sulfidation as exemplified by the data of Table 9. Alloy A experiences rapid liquid phase degradation in H_2 - 45%CO_2 – 1% H_2 at 816°C in approximately 30 hours. The remaining alloys showed gradual

improvement as the zirconium content was raised but became dramatically resistant to sulfidation above about 0.015% (150 ppm) zirconium. Examination of the compositions tested suggest that yttrium plays a minor positive role in enhancing sulfidation resistance, but is unable to dramatically effect sulfidation resistance. Alloys containing more than 0.015 weight percent (150 ppm) zirconium have been tested in the above environment for nearly 1.5 years (12,288 hours) without failure.

Table 9
Effect of Zirconium Content on the Sulfidation Resistance of the Alloys of H_2 - 45%CO_2 - 1%H_2 at 816°C

Alloy	Zirconium Content (%)	Mass Change at 168 Hours (mg/cm^2)	Mass Change at Test Termination (Hours)	(mg/cm^2)
1	0.018	0.30	12,288	3.91
3	0.012	4.30	168	4.30
4	0.21	0.41	12,288	3.08
5	0.21	0.41	12,288	2.70
8	0.010	2.17	168	2.17
9	0.031	0.51	12,288	3.64
A	None	30.82	168	30.82

NITRIDATION RESISTANCE

The zirconium-containing alloy also has outstanding resistance to nitridation as measured in pure ammonia at 1100°C. Data to 1056 hours are presented in Table 10. These data show that alloy B (low in aluminum) alloys containing 3 weight percent aluminum but no zirconium or yttrium (such as alloy C) and alloys containing only yttrium (such as alloy 13) possess good but not outstanding resistance to nitridation. Alloys 3 and 8, containing at least 2.75 weight percent aluminum and greater than 0.01 weight percent (100 ppm) each of zirconium and yttrium, possess outstanding resistance to nitridation.

Table 10
Effect of Zirconium and Yttrium on Nitridation Resistance in Pure Ammonia at 1100°C
Mass Change (mg/cm^2)
Time in Hours

Alloy	240	312	504	552	720	768	1032	1056
3	--	0.47	--	0.55	0.62	--	--	0.68
8	--	0.48	--	0.55	0.63	--	--	0.70
13	6.17	--	9.91	--	--	11.58	12.75	--
B	4.42	--	7.33	--	--	8.70	10.03	--
C	6.02	--	9.76	--	--	11.46	12.68	--

This alloy range has maximum corrosion resistance to a broad range of aggressive high temperature environments. The alloy's properties are suitable for multiple high temperature corrosion applications, such as, regenerators, recuperators, combustors and other gas turbine components, muffles and furnace internals, retorts and other chemical process equipment and transfer piping, boiler tubing, piping and waterwall aprons and waste incineration hardware. Furthermore, a combination of γ', carbide precipitation and solid solution hardening provides a stable structure with the requisite strength for these high temperature corrosion applications.

In accordance with the provisions of the statute, the specification illustrates and describes specific embodiments of the invention. Those skilled in the art will understand that changes may be made in the form of the invention covered by the claims that certain features of the invention may sometimes be used to advantage without a corresponding use of the other features.

We claim:

1. A nickel-base alloy consisting of in weight percent, about 42 to 58 nickel, about 21 to 28 chromium, about 12 to 18 cobalt, about 4 to 9.5 molybdenum, about 2 to 3.5 aluminum, about 0.05 to 2 titanium, at least one microalloying agent selected from the group consisting of about 0.005 to 0.1 yttrium and about 0.01 to 0.6 zirconium, about 0.01 to 0.15 carbon, about 0 to 0.01 boron, about 0 to 4 iron, about 0 to 1 manganese, about 0 to 1 silicon, about 0 to 1 hafnium, about 0 to 0.4 niobium, about 0 to 0.1 nitrogen, incidental impurities and deoxidizers.

2. The nickel-base alloy of claim 1 containing about 8 to 20 weight percent γ' phase.

3. The nickel-base alloy of claim 1 containing less than about 2 weight percent γ'' phase.

4. The alloy of claim 1 including about 43 to 57 nickel, about 21.5 to 27 chromium, about 12.5 to 17.5 cobalt and about 4.5 to 9 molybdenum.

5. The alloy of claim 1 including about 2.25 to 3.5 aluminum and about 0.06 to 1.6 titanium.

6. The alloy of claim 1 including about 0.01 to 0.5 zirconium, about 0.01 to 0.14 carbon and about 0.0001 to 0.01 boron.

7. A nickel-base alloy consisting of in weight percent, about 43 to 57 nickel, about 21.5 to 27 chromium, about 12.5 to 17.5 cobalt, about 4.5 to 9 molybdenum, about 2.25 to 3.5 aluminum, about 0.06 to 1.6 titanium, at least one microalloying agent selected from the group consisting of about 0.01 to 0.08 yttrium and about 0.01 to 0.5 zirconium, about 0.01 to 0.14 carbon, about 0.0001 to 0.01 boron, about 0 to 3 iron, about 0 to 0.8 manganese, about 0.01 to 1 silicon, about 0.01 to 0.8 hafnium, about 0.00001 to 0.08 nitrogen, incidental impurities and deoxidizers.

8. The nickel-base alloy of claim 7 containing about 8 to 20 weight percent γ' phase.

9. The nickel-base alloy of claim 7 containing less than about 2 weight percent γ'' phase.

10. The alloy of claim 7 including about 44 to 56 nickel, about 22 to 27 chromium, about 13 to 17 cobalt and about 5 to 8.5 molybdenum.

11. The alloy of claim 7 including about 2.5 to 3.5 aluminum and about 0.08 to 1.2 titanium.

12. The alloy of claim 7 including about 0.02 to 0.5 zirconium, about 0.01 to 0.12 carbon and 0.01 to 0.009 boron.

13. A nickel-base alloy consisting of in weight percent, about 44 to 50 nickel, about 22 to 27 chromium, about 13 to 17 cobalt, about 5 to 8.5 molybdenum, about 2.5 to 3.5 aluminum, about 0.08 to 1.2 titanium, about 0.01 to 0.07 yttrium, about 0.02 to 0.5 zirconium, about 0.01 to 0.12 carbon, about 0.001 to 0.009 boron, about 0.1 to 2.5 iron, about 0 to 0.6 manganese, about 0.02 to 0.5 silicon, about 0 to 0.7 hafnium, about 0.0001 to 0.05 nitrogen, incidental impurities and deoxidizers.

14. The nickel-base alloy of claim 13 containing about 8 to 20 weight percent γ' phase.

15. The nickel-base alloy of claim 13 containing less than about 2 weight percent γ'' phase.

16. The alloy of claim 13 including about 45 to 55 nickel, about 22 to 26 chromium, about 14 to 16 cobalt and 5 to 8 molybdenum.

17. The alloy of claim 13 including about 2.75 to 3.5 aluminum and about 0.1 to 1 titanium.

18. The alloy of claim 13 including about 0.01 to 0.06 yttrium, about 0.02 to 0.4 zirconium, about 0.02 to 0.1 carbon and about 0.003 to 0.008 boron.

19. The nickel base alloy of claim 13 containing about 2.75 to 3.5 aluminum, about 0.003 to 0.008 boron, about 0.02 to 0.1 carbon, about 14 to 16 cobalt, about 22 to 26 chromium, about 0.5 to 2 iron, about 0 to 0.5 hafnium, about 5 to 8 molybdenum, about 0.01 to 0.05 nitrogen, about 0 to 0.2 niobium, about 45 to 55 nickel, about 0.05 to 0.4 silicon, about 0.1 to 1 titanium, about 0.01 to 0.06 yttrium and about 0.02 to 0.4 zirconium.

ADVANCED HIGH TEMPERATURE CORROSION RESISTANT ALLOY

ABSTRACT

A nickel-base alloy consisting of, in weight percent, 42 to 58 nickel, 21 to 28 chromium, 12 to 18 cobalt, 4 to 9.5 molybdenum, 2 to 3.5 aluminum, 0.05 to 2 titanium, at least one microalloying agent selected from the group consisting of 0.005 to 0.1 yttrium and 0.01 to 0.6 zirconium, 0.01 to 0.15 carbon, 0 to 0.01 boron, 0 to 4 iron, 0 to 1 manganese, 0 to 1 silicon, 0 to 1 hafnium, 0 to 0.4 niobium, 0 to 0.1 nitrogen, incidental impurities and deoxidizers.

Practitioner's Docket No. PC-3201/USA **PATENT**

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- [XX] original.
- [ ] design.
- [ ] supplemental.

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

- [ ] national stage of PCT.

NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.

- [ ] divisional.
- [ ] continuation.
- [ ] continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor *(if only one name is listed below)* or an original, first and joint inventor *(if plural names are listed below)* of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

ADVANCED HIGH TEMPERATURE CORROSION RESISTANT ALLOY,

SPECIFICATION IDENTIFICATION

the specification of which:

(complete (a), (b) or (c))

(a) ☒ is attached hereto.

NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____, as ☐ Serial No. 0 /_____ or ☐ _____ and was amended on _____ *(if applicable).*

NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.

NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:

"(1) name of inventor(s), and application number (consisting of the series code and the serial number; e.g.,08/123,456);

"(2) name of inventor(s), serial number and filing date;

"(3) name of inventor(s) and attorney docket number which was on the specification as filed;

"(4) name of inventor(s), title which was on the specification as filed and filing date;

"(5) name of inventor(s), title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or

"(6) name of inventor(s), title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number; e.g.,08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."

Notice of July 13, 1995 (1177 O.G. 60).

(c) ☐ was described and claimed in PCT International Application No. _____, filed on _____ and as amended under PCT Article 19 on _____ *(if any).*

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

☒ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

PRIORITY CLAIM (35 U.S.C. § 119(a)-(d))

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

(d) ☒ no such applications have been filed.

(e) ☐ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.

PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)

COUNTRY (OR INDICATE IF PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐

CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(34 U.S.C. § 119(e))

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER	FILING DATE
_____ /_____	_____
_____ /_____	_____
_____ /_____	_____

CLAIM FOR BENEFIT OF EARLIER US/PCT APPLICATION(S) UNDER 35 U.S.C. 120

☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN PART (C-I-P) APPLICATION.

ALL FOREIGN APPLICATION(S), *IF ANY*, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

NOTE: *If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.*

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

EDWARD A. STEEN - ASSISTANT GENERAL COUNSEL - PATENTS - REG. NO.: 28,909
BLAKE T. BIEDERMAN - ATTORNEY - REG. NO.: 34,124

(check the following item, if applicable)

☐ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

☒ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

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DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other documents.

Full name of sole or first inventor

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(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST NAME))

Inventor's signature

Date **Country of Citizenship**

Residence

Post Office Address

(check proper box(es) for any of the following added page(s) that form a part of this declaration)

☐ **Signature** for fourth and subsequent joint inventors. *Number of pages added* _____.

* * *

☐ **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____.

* * *

☐ **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. *Number of pages added* _____

* * *

☐ Added page for **signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

* * *

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

* * *

☐ Authorization of practitioner(s) to accept and follow instructions from representative.

* * *

(if no further pages form a part of this Declaration, then end this Declaration with this page and check the following item)

☒ This declaration ends with this page.